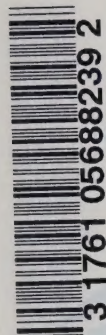


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Report: AQRB-83-009T

A LITERATURE REVIEW OF OZONE
IN THE ATMOSPHERE
AND
AN INTERPRETATION
OF EXCEPTIONALLY HIGH VALUES
OF SURFACE OZONE
RECORDED AT REGINA, SASKATCHEWAN

(completed: December 1983)

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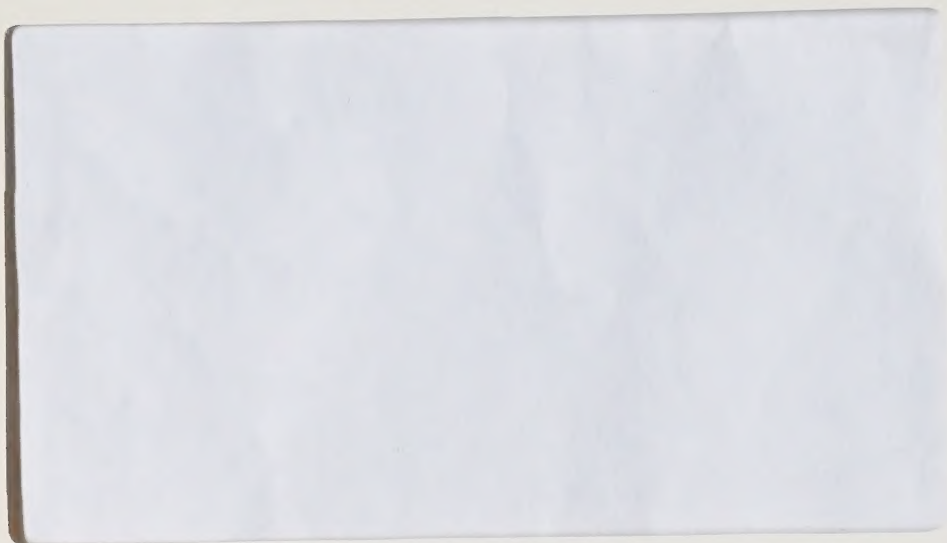


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OF EXCEPTIONALLY HIGH VALUES
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(completed: December 1983)

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RÉSUMÉ

L'étude des sources et des puits d'ozone (O_3) atmosphérique n'est pas chose facile. En effet, la teneur en ozone de l'atmosphère est faible et variable, ce qui rend difficile la mesure de cet élément. Si nous voulons déterminer les effets des sources naturelles sur le degré de concentration de l'ozone au niveau du sol, il nous faut approfondir notre connaissance du comportement de l'ozone atmosphérique.

Nous avons examiné les ouvrages sur l'ozone atmosphérique et la météorologie en concentrant nos recherches sur les intrusions d'ozone stratosphérique au niveau du sol. Nous avons déduit de cette étude que les conditions atmosphériques influent grandement sur la distribution de l'ozone dans l'atmosphère. Les teneurs moyennes d'ozone observées dans les injections stratosphériques au niveau de la couche limite planétaire sont en général inférieures à environ 35 ppb. On peut considérer cette valeur comme niveau "naturel" dans la couche limite planétaire et donc comme base de comparaison dans les cas d'épisodes de fortes concentrations d'ozone.

L'examen des valeurs exceptionnellement élevées, observées au niveau du sol à Regina (Saskatchewan), nous porte en outre à penser qu'elles correspondent à des affaissements d'air stratosphérique. Les cas de fortes concentrations d'ozone (plus de 120 ppb près du sol), résultant d'intrusions stratosphériques, semblent être des phénomènes localisés assez rares, malgré la fréquence des creux barométriques en altitude et la prédominance des courants-jets. Ces épisodes ont une durée caractéristique de une à trois heures.

ABSTRACT

The study of sources and sinks of atmospheric ozone (O_3) has remained a difficult task simply because of the small and variable concentrations of O_3 in the atmosphere and because of the difficulty of making measurements. A more complete understanding of the behaviour of atmospheric O_3 must be sought in order to determine the impact of natural sources on measured O_3 concentrations at ground level.

A review of the available literature on atmospheric O_3 and associated meteorology has been carried out with emphasis placed on stratospheric O_3 intrusions to ground level. The review indicates that meteorology plays a major role in the distribution of O_3 in the atmosphere. Observed mean O_3 concentrations due to stratospheric injections to the planetary boundary layer (PBL) are generally less than ~ 35 ppb. This value can be considered a natural "background level" in the PBL and a basis against which episodes of high O_3 concentrations can be compared.

In addition, an examination of exceptionally high O_3 values recorded at the ground level in Regina, Saskatchewan suggested that they were due to downward transport from the stratosphere. The occurrence of high O_3 concentrations (in excess of 120 ppb near the ground) due to stratospheric intrusion appears to be an uncommon local phenomenon, even with the frequent passages of upper troughs and the prevalence of jet streams etc. Characteristically, such O_3 episodes are observed to last only one to three hours.

ABSTRACT

The study of aerosols and their atmospheric behavior (log) has remained a difficult task since the early and variable concentrations of O_3 in the atmosphere and the difficulty of making measurements. A more complete understanding of the behavior of atmospheric O_3 must be sought in order to determine the impact of aerosols on various concentrations at ground level.

A review of the available literature on atmospheric O_3 and associated meteorology has been carried out with special regard to atmospheric O_3 literature at ground level. The

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In addition, an examination of exceptionally high O_3 values recorded at the ground level in Regina, Saskatchewan suggested that they were due to downward transport from the stratosphere. The occurrence of high O_3 concentrations in excess of 100 ppb near the ground due to stratospheric intrusion appears to be an uncommon local phenomenon, even with the transport of upper tropospheric and stratospheric air masses. Characteristically, such high values are observed in late May or in other months.

1. INTRODUCTION

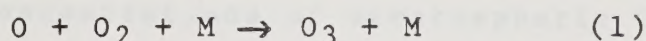
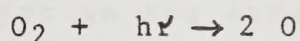
Since Schönbein (1840) discovered the gas ozone (O_3), numerous researchers have devoted their efforts to the investigation of the sources and sinks and to understanding the overall behaviour of atmospheric O_3 . O_3 is a minor gaseous constituent of the lower atmosphere in comparison with N_2 (78%), O_2 (21%), Ar (<1%) and CO_2 (~ 0.03%), and it is considered one of the major pollutants in the planetary boundary layer (PBL). Exceedances of established air quality standards for ozone have been reported from all parts of the globe. Since ozone at concentrations of 100-200 ppb can aggravate respiratory diseases, damage vegetation, reduce crop yields and damage many materials, considerable efforts have been expended in attempting to control O_3 concentration levels in the PBL. Because of the complexity of its behaviour and its environmental impacts, the study of atmospheric O_3 is, and will remain to be, a challenging subject during the forthcoming years.

The formation, transport and build-up of O_3 in the atmosphere have been the subject of numerous studies during the last three decades (e.g., Junge, 1962; Aldaz, 1969; Dütsch, 1978). O_3 is found abundantly in the so-called ozonosphere at the 12-35 km level of the lower stratosphere, as shown in Fig. 1. Junge (1963) and Hering (1966) have shown that a very substantial amount of O_3 is transported annually from the stratosphere down to the ground level where it is destroyed by reaction with the ground cover and aerosols. The main sink of atmospheric O_3 is therefore known to be the earth's surface where its molecules are reduced by chemical contact. Aldaz (1969) estimated that O_3 is destroyed over grassland roughly 15 times faster than over sea water and that the continents destroy most of the tropospheric O_3 . The ocean spray layer consists of water and salt particles and these particles are also effective in destroying O_3 (Fabian and Junge, 1970). In addition, water droplets in clouds and precipitation, i.e. relative humidity 100%, are another efficient agent for the destruction of O_3 .

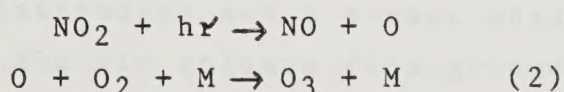
According to our review of the available literature, O_3 in the atmosphere can be generally said to have three source regions: (1) stratosphere, (2) upper and mid-troposphere, and (3) lower troposphere - PBL. It is the purpose of this paper to present a review of relevant studies of atmospheric ozone with particular emphasis on the transport of stratospheric O_3 into the PBL atmosphere. An assessment of the background level of O_3 in the PBL due to natural sources has been carried out. In addition, a meteorological interpretation of the exceptionally high O_3 values recorded at Regina, Saskatchewan during the period of 26-28 December 1980 is described in Section 5.

2. STRATOSPHERIC OZONE AND ITS TRANSPORT

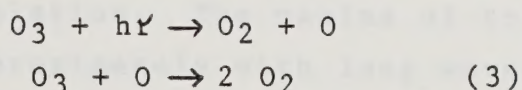
Under conditions existing in the stratosphere, the photochemical theory introduced by Chapman (1930) provides the following processes:



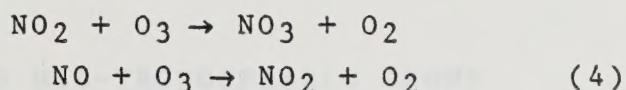
The above reactions result in the formation of O_3 in the stratosphere. These processes occur very quickly (~ 15 minutes) with the aid of sunlight and a third body (M) (Junge, 1963). When nitrogen oxides are present in the atmosphere, O_3 may occur with the following reaction scheme:



In the stratosphere O_3 plays an important role in shielding the earth's surface from solar uv radiation. Ozone destruction schemes, on the other hand, are given by the following:



These reactions are known to occur very slowly with the transformation between O and O_3 occurring continually in the atmosphere (Dütsch, 1969). A recent study (Johnston and Whitten, 1973) has shown that O_3 destruction by these reactions accounts for only 20% of the total destruction. Other schemes include destruction of O_3 with H O_2 (Hov, 1983), when levels of NO_x are extremely low. The destruction mechanism with NO_x involves the following fast processes:



Dütsch and Ling (1973) have shown that a pronounced O_3 partial pressure maximum (180 nb) in vertical ozone distribution occurs in March while a minimum generally takes place in October, as shown in Fig. 2. The O_3 maximum is found at the level between 18 - 24 km and the minimum at about 6-7 km over Arosa, Switzerland. The warmest layer in the stratosphere is around the 48 km level and apparently this altitude does not coincide with the level of maximum concentrations of stratospheric O_3 . By referring to Fig. 3, it can be seen that there are actually three O_3 maxima in the Northern Hemisphere; the first one is over the northern section of Hudson Bay, the second over Manchuria and the third over western Europe (London et al., 1976).

Dütsch (1969; 1978) has stated that photochemical theory predicts a decrease in total O_3 in the atmosphere from the equator toward higher latitudes; and a summer maximum and winter minimum of total O_3 in the air columns from ground level to the top of the atmosphere. Measurements show that the lowest values, however, are found in the tropical regions without significant changes throughout the year. It has been suggested that observed O_3 maxima are the results of a net poleward transport of O_3 by the mean-meridional circulation. The maxima of total atmospheric O_3 appear to coincide approximately with long wave troughs of 500 mb (Schlesinger and Mintz, 1979) or 250 mb height fields.

Aircraft and balloon measurements of O_3 in the lower stratosphere in excess of 500 ppb have been reported by many researchers (e.g., Danielsen and Mohnen, 1977; Dutkiewicz and Husain, 1979; WMO, 1982). By considering the general circulation and the distribution of O_3 maxima and of thermal regimes (i.e. gaps and discrepancies) in the stratosphere, it is clear that our understanding of the behaviour of O_3 in the upper atmosphere could be much improved.

3. UPPER AND MID-TROPOSPHERIC OZONE

Palmén and Newton (1969, p. 176) have shown the circulation structure of an upper atmospheric system including the tropopause and frontal surface, as can be seen in Fig. 4. The distribution of O_3 and its transport in the troposphere depends on the general circulation of the troposphere and stratosphere as a coupled system. In the ozonosphere the gradient of O_3 mixing ratio is evidently large and concentrated from about 25 km down to the tropopause. The O_3 -rich air in the lower stratosphere can be transported downward into the troposphere by large-scale amplifying waves and upper troughs, especially in the cold air (west) side of a frontal system as illustrated in Fig. 4. Therefore, measurements of tropospheric O_3 (and 7Be) are often used to trace stratospheric and tropospheric exchanges.

Stratospheric O_3 may subside into the troposphere when vertical eddy fluxes occur. In particular, large-scale turbulent motion develops near an upper trough and stratospheric O_3 is transported through a break in the tropopause. Thus Danielsen (1968) has demonstrated that O_3 is transported and mixed into the troposphere by the tropopause folding phenomenon, and stated that the tropopause is a transition region between the chemically active stratosphere and the dynamically active troposphere. As shown in Fig. 5, he has suggested that intermittent transfer of stratospheric O_3 into the troposphere occurs during a period of tropopause folding, and that descending air is a cause for observed high concentrations in the troposphere. Because of the

transport mechanism with advection and subsidence, many investigators (e.g., Dütsch, 1969) have pointed out that the tropospheric maximum is delayed into summer months.

In support of this transport mechanism, Fabian and Pruchniewicz (1977) obtained aircraft measurements of O_3 that occurred by stratospheric injections at about 30° , 45° and 65° N. Nastrom (1977) also used O_3 data, measured using commercial airliners, to estimate the vertical and horizontal O_3 fluxes near the tropopause. A significant O_3 variation near the tropopause was found to be about 1,900 km long. He suggested that the amount of O_3 in the troposphere was essentially controlled by the direct intrusion of O_3 - rich air from the stratosphere. As shown in Fig. 6, Danielsen and Mohnen (1977) measured 225-500 ppb of O_3 in the upper troposphere and lower stratosphere, and stated that 600-1,000 ppb could be measured at the higher level. Danielsen (1980) also measured mid-tropospheric O_3 values from aircraft surveys in the range of 80-100 ppb at about the 5 km level. When an upper trough was favourable, however, O_3 values exceeding 250-300 ppb were found at the 6.5 km level. In the mid-troposphere, Singh et al. (1980) also found O_3 levels as high as 300 ppb within a stratospheric intrusion. Johnson and Viezee (1981) observed a peak O_3 concentrations at high altitudes in the range of 240-400 ppb and decreasing to 100-200 ppb at lower altitudes (Table 1). They pointed out that O_3 -rich air was transported into the troposphere with each intense cyclone development and with virtually every trough. The stratospheric intrusions occurred more frequently than other studies had indicated. Over the central U.S. in spring and fall of 1978, stratospheric injections were typically "100-300 km wide and several hundreds of kilometer long". They also stated that they were able to track intrusions down as far as the top of the PBL, as illustrated in Fig. 7.

On the top of an isolated mountain, the daily O_3 maximum occurs around mid-night or at daybreak while the minimum

tends to occur at noon. In contrast, maximum O_3 concentrations on flat terrain generally take place shortly after noon. Reiter et al. (1977) reported that at the 3-km peak of the Zugspitze Mountain, daily mean values of O_3 measured were in the range of 50-60 ppb. They also measured maximum one-hour concentrations of O_3 in excess of 145 ppb during a period of 6 hours around midnight of January 8-9, 1975.

4. OZONE IN THE PLANETARY BOUNDARY LAYER

(a) Stratospheric Ozone Intrusion to Ground Level.

Up until the late 1960's, O_3 measurements in the PBL greater than 60 ppb were attributed to stratospheric injections. As noted earlier, many scientists thought that stratospheric O_3 leaks into a tropopause gap (Junge, 1962). For example, Stickse (1975) presented arguments that O_3 concentrations in the stratosphere are up to 100 times more than those obtained at ground level, and all the measured values at the surface could be explained in terms of stratospheric intrusions. Stasiuk and Coffey (1974) also indicated that high O_3 concentrations near ground level were not the result of photochemical reaction of air pollutants at this level but they were exclusively the result of a common source from the ozonosphere. They explained observed high values and daily maximum values at the ground level in terms of mere vertical mixing. Such conclusions were generally drawn from examinations of vertical O_3 profiles.

Interaction of cosmic rays with N_2 , O_2 , Ar etc. produce large amounts of radioactive isotopes such as 7Be and ^{90}Sr . Junge (1962) suggested the use of radionuclides to trace the circulation exchanges between stratosphere and troposphere. Several studies (e.g., Ludwick et al., 1976; Dutkiewicz and Husain, 1979; Husain et al., 1977) have shown the viability of using 7Be as a radioactive tracer to identify stratospheric O_3 at ground level. Danielsen and Mohnen (1977) have discussed the positive correlation between O_3 and potential

vorticity and between potential vorticity and ^{90}Sr . According to their study, O_3 of stratospheric origin was injected into the troposphere when the boundary between the stratosphere and the troposphere deformed and became vertical in the core of a jet stream.

Many studies (e.g., Ludwick et al., 1976; Reiter et al., 1977; Viezee and Singh, 1980) found positive correlation on a daily basis between levels of O_3 and ^7Be at the ground with changes in synoptic motion systems. As shown in Fig. 8, Dutkiewicz and Husain (1979) measured elevated O_3 concentrations with high values of ^7Be . At Whiteface Mountain in New York State observed average concentrations of ^7Be were only about one tenth of those measured in the stratosphere. The ^7Be peaks were in good agreement with an increase in O_3 concentrations at the ground level. Thus it was concluded that the high values of ^7Be were the result of stratospheric air reaching the lower troposphere, since there were no ground-based ^7Be sources. However, the radionuclide is now considered a natural constituent in the troposphere (Viezee and Singh, 1980). It is recognized that as much as 40% of the ^7Be observed in the lower atmosphere is of tropospheric origin. Therefore, earlier observations made for O_3 and ^7Be , or other radionuclides, do not necessarily provide conclusive evidence on their stratospheric origins.

A number of exceptionally high O_3 values, exceeding 200 ppb near the ground, have been reported and explained in terms of natural intrusions. Attmannspacher and Hartmannsgruber (1973) reported extremely high O_3 readings (250-500 ppb) at the top of a 1-km high mountain in Germany. Their study indicated that these readings occurred in connection with cold fronts, and that snow and a thunderstorm were occurring during the high O_3 event. Lamb (1977) also found high O_3 concentrations (230 ppb) at Santa Rosa, California during the hour 0300-0400 LST, 19 November, 1972.

The strip charts from the Santa Rosa O₃ recorder showed three peaks during seven hours. The examination of O₃ data from the intense monitoring network around San Francisco and in northern California indicated that the exceptionally high values occurred only at Santa Rosa. He suggested that the O₃ responsible for the anomalous concentrations came from the stratosphere with downdrafts and precipitation and not from anthropogenic sources. He raised, however, a question of why O₃ anomalies were not observed at any of the other stations that reported precipitation. In another study, exceptionally high O₃ values observed at the ground level in Denver, Colorado were reported by Haagenson et al. (1981). On the afternoon of 4 March 1978, O₃ concentrations of 223 ppb were recorded at Denver; the event was explained in terms of enhanced photochemistry together with O₃ transport from the stratosphere.

From investigations of meteorological and O₃ data, maximum ground level O₃ concentrations due to stratospheric O₃ intrusions have been estimated to be ~ 35 ppb (Chung, 1977; Yap and Chung, 1977). The estimation was made over the area generally influenced by the cold-fresh air and subsidence in air columns of anticyclones. Frequently, daily maxima less than 20 ppb were recorded at many Canadian stations in such synoptic situations. Dutkiewicz and Husain (1979) determined stratospheric O₃ injection at Whiteface Mountain, N.Y. to vary between 19-47 ppb for June and July 1977. Husain et al. (1977) also estimated that stratospheric O₃ contributions to ground level concentrations to be less than 37 ppb. Wolff et al. (1979) indicated that mean surface O₃ concentrations attributed to stratospheric intrusions were between 15-50 ppb. From another report, Singh et al. (1980) estimated background levels of O₃, principally of stratospheric origin, to be 50, 40 and 30 ppb for spring, summer and fall, respectively.

Further examinations of hourly O₃ data for Ontario and other provinces for the years of 1976-82 support the earlier

observations of a background level of about 35 ppb. Such low values occur on the arrival of new anticyclones after cold frontal passages and can be used as a comparison to episode cases of high O_3 levels. The newly arrived cold, clean air, i.e. cold air outbreak in the forward side of an anticyclone, pushes and sweeps away polluted- O_3 -rich air to the east or southeast.

When a cyclone is fully developed, the slope of a cold frontal surface is steep and the separation distance between the surface low and an upper cold low or trough is normally short, 500 km or less, in eastern North America (Chung and Reinelt, 1973). In the west side of an upper trough, the general subsidence and confluence aloft would enhance downdrafts in the direction of a cold frontal surface. This motion system in turn generates a strong descending current vertically in the forward side of an anticyclone and provides a favourable condition for O_3 -rich air from the stratosphere to be brought down to the PBL. In other words, the low concentrations observed of ~ 35 ppb or less in the forward side of anticyclones (i.e. SE to NE quadrant) are mainly due to vertical transport from the ozonosphere and are often referred to as the natural "background" level near the ground surface.

From the studies discussed above it is clear that estimations of hourly O_3 maximum at the ground level due to the direct contribution of stratospheric O_3 -rich air are usually in the range of 20-50 ppb.

(b) Formation of Ozone at the Ground Level.

Junge (1962) showed that O_3 is fairly uniformly distributed in the troposphere, and that tropospheric O_3 is a more regular phenomenon than previously considered. He explained that destruction of O_3 occurs in polluted air and also that O_3 can be formed by photochemical reactions among pollutants in cities such as Los Angeles, California. At ground level O_3 values higher than 45 ppb were not thought to be common.

except for polluted atmosphere like Los Angeles where 500 ppb and more could be expected. Interestingly, Junge also placed some emphasis on the exchange scheme of O_3 , CO_2 and CH_4 .

Chameides and Walker (1973) pointed out that O_3 is in photochemical equilibrium in the troposphere and that its distribution and variations are mostly determined by photochemistry. Crutzen (1974) was among the first who suggested that appreciable amounts of O_3 are destroyed and produced in the troposphere by chemical reaction of CH_4 and NO_x . In turn, naturally occurring chemical components plus anthropogenic pollutants in the troposphere could act as precursors of O_3 . His concept also suggests a possibility of O_3 sinks due to gas phase photolytic destruction in the troposphere. The earlier destruction schemes suggested O_3 sinks only near ground level.

Ripperton et al. (1971) also demonstrated the formation of small O_3 concentrations in the air at ground level. Crutzen (1974) suggested that tropospheric generation may contribute significantly to the total O_3 in the atmosphere. Davies et al. (1974) found significant O_3 production in plumes far downstream from a large power plant and indicated that photochemical reactions do account for the increase in O_3 values. In another study, Fishman and Crutzen (1978) proposed that CO oxidation in the presence of NO is a significant source of tropospheric O_3 . From theoretical studies, Calvert (1976) and Seinfeld (1977) were able to confirm the mechanism of O_3 formation at the ground level with polluted air in Los Angeles.

Near the ground surface, daily O_3 maximum occurs shortly after noon and usually decreases to a minimum at dawn. In contrast, the maximum at sea takes place during night-time (Stallard et al., 1975). Since radiation inversion is rare both at sea and at the mountain top, the night-time maxima may be explained with the lowering of PBL and subsidence during that time. Over flat terrain, however, convection and eddy motion are

generally strong after noon and overall mixing of the air occurs in the PBL. The usual explanation for O_3 maximum during afternoon hours is the downward transport and convective mixing of the air within the boundary layer. Nevertheless, it is found that the mixing mechanism provides O_3 with a greater chance of chemical contact with the earth's surface. Destruction at the surface is a mechanism of O_3 dissipation suggested by earlier researchers. This in turn suggests that O_3 is produced by photochemical reactions at a faster and greater rate than it is being destroyed by chemical contact at the ground.

Coffey and Stasiuk (1975) interpreted urban O_3 peak concentrations as primarily the result of high background levels of O_3 and not local photochemical generation, even though urban peaks such as in Los Angeles have been generally explained as the results of a photochemical situation. In eastern North America the highest O_3 concentrations were recorded when winds were from the south and southwest (Coffey and Stasiuk, 1975; Chung, 1976; Samson and Ragland, 1977), while decreasing values were found when winds shifted to the northwest with cold frontal passages.

Air pollutants may be transported over long distances and observed values of photochemical O_3 increase downwind from large urban areas (Cleveland et al., 1976). From examinations of a few years of meteorological charts, high O_3 values exceeding 80 ppb were usually found with warm-moist air in the rear (back) side of an anticyclone and in the warm sector of a cyclone (Yap and Chung, 1977; Schjoldager, 1979). Aircraft surveys done in the PBL also suggested that urban O_3 was well mixed and spread over wide areas by turbulent processes of the air currents (Lusis et al., 1976). It was found that maximum O_3 concentrations produced by photochemically active precursors from large urban and regional sources were about 250 ppb at the 1-km altitude.

Ambient temperatures have been shown to increase markedly whenever the level of surface O_3 is very high and vice versa (Chung, 1977). It is understood that solar uv radiation is

absorbed by O_3 . To date the resultant absorption mechanism and the impact of increased ambient temperature by O_3 in the PBL are not well understood, and numerical studies are needed to gain a better understanding of the behaviour of O_3 in the lower atmosphere.

5. OBSERVATIONS OF EXCEPTIONALLY HIGH VALUES OF SURFACE OZONE

During the period 26-28 December 1980, exceptionally high values of O_3 were recorded at the ground level in Regina, Saskatchewan. Initially, these unusual recordings were treated as erroneous data caused by instrument malfunction or operator error. From the review of earlier studies on stratospheric O_3 intrusion and from a closer examination of meteorological records, we now have concluded that the exceptionally high O_3 values which occurred at Regina were the result of stratospheric intrusion of O_3 -rich air to ground level. Associated meteorology prior to and after the event occurrence is described in this Section. The anomalous O_3 values recorded at Regina were in the form of three impulsive peaks as follows (Fig. 9):

- (I) 92 ppb at 2300 LST, 26 December 1980.
- (II) 138-228 ppb during 1800-2000 LST, 27 December 1980.
- (III) 146 ppb at 0100 LST, 28 December 1980.

The O_3 monitoring instrument in Regina was a Bendix Model 8002 and used the gas phase chemiluminescent ethylene/ozone detection principle. The monitor had undergone functional and zero/span checks both prior to and following the ozone event and no abnormalities had been detected.

(a) Associated Meteorological Conditions

Peak I (92 ppb)

- 1) The occurrence of snow with low clouds.
- 2) A general warming trend with the approach of a pronounced warm (quasi-stationary) front.

- 3) An increase in air temperatures during the afternoon hours from -15.2°C to -6.7°C , and then nearly no-change in temperatures for ten hours before the event occurrence of high O_3 .
- 4) Regina was in close proximity, within about 100 km, of a warm front (i.e. south of Regina).
- 5) A wind shift with strong winds from SE to SW.
- 6) Intensification of a surface trough.
- 7) Passage of a warm front at 0200 LST, 27 December (Fig. 10).
- 8) An upper ridge over Saskatchewan at the 500 and 250 mb levels (0600 LST, 27 Dec.)
- 9) A strong jet stream over Saskatchewan; 158 km h^{-1} at 500 mb and 222 km h^{-1} at 250 mb.

The first anomalous peak occurred three hours prior to the warm front passage.

Peak II (138-228 ppb)

- 1) Regina was in the warm sector of an intense Alberta low.
- 2) A period of very warm air (3.5 to 8.2°C) during the day-time hours on 27 December and then
- 3) A sudden decrease in air temperature (8.2 to 2.2°C) at 1700 LST, 27 December.
- 4) The occurrence of light rainshowers (NB. -36.9°C on 24 December) from stratocumulus and altocumulus clouds.
- 5) A marked shift in winds from SW to W.
- 6) Passage of a cold front at 1700 LST, 27 December.
- 7) The presence of a minor short-wave trough at 250 mb over Sask. at 1800 LST.
- 8) The passage of a short-wave trough at the 500 mb level via Sask. and situated over Manitoba at 1800 LST (Fig. 11).
- 9) A strong jet stream over Sask.; 148 km h^{-1} at 500 mb and 222 km h^{-1} at 250 mb.

The high O_3 values occurred one hour after the passage of the cold (quasi- stationary) front with brief and light rainshowers which might indicate subsidence.

Peak III (146 ppb)

- 1) A wind shift from NW to SW when the O_3 values reduced, and then a wind shift to steady westerlies from 0200 LST, 28 December.
- 2) Clear skies with westerlies (subsidence).
- 3) A steady decrease in ambient temperatures.
- 4) The presence of a cold (quasi-stationary) front over Regina, which passed to southward at 0200 LST.
- 5) Sask. was under the influence (west side) of a 500 mb trough (0600 LST 28 December).
- 6) A strong jet stream over Sask.; 102 km h^{-1} at 500 mb and 130 km h^{-1} at 250 mb.

The O_3 peak value occurred one hour before the passage of a cold front.

(b) Discussion

In general there were significant changes in meteorological conditions at Regina during the events of spurious O_3 readings. The following conditions are particularly noteworthy: 1) The presence of a quasi-stationary (warm and cold) front with the formation of a lee cyclone, 2) the approach of an upper trough, 3) a period of sudden warming after a prolonged spell of very cold weather (i.e. from -36.9°C to 8.2°C) and then a rapid drop in air temperature with the cold frontal passage, 4) wind shifts, variable cloudiness and brief rainshowers in winter, 5) the formation and the passage of an upper trough, and 6) the presence of a strong jet stream maximum at all levels from 850 to 250 mb over southern Saskatchewan.

Apparently, the jet stream maximum (111 km h^{-1}) at 850 mb passed through the Regina area at about 1600 LST, 27 December, while jet stream maxima at both 700 and 500 mb were situated over Regina at about 1700 LST of the same day. At the 250 mb level, however, the maximum (222 km h^{-1}) of a jet stream was right over Regina at 1800 LST, and the city was under the influence of the east side of a 250 mb trough. The phase lag, separation distance,

between the surface cyclone and 700 mb trough was less than 200 km, indicating that the frontal slope was steep and extended nearly vertically between these levels. The separation distances from surface to 500 and 250 mb levels were about 500 and 1,000 km, respectively. These are typical separation distances for fast moving lee cyclones with the slope of a cold front of 1:100. The upper air data of a neighboring station (The Pas) suggested that the height of the tropopause was at the 191 mb (~ 12.1 km) level around 1800 LST, 27 December, and that it had lowered to 279 mb (9.6 km) altitude at 0600 LST of the following day after the passage of a short wave trough at the 250 mb level. In other words, O_3 maximum of 228 ppb at the ground level in Regina occurred under the core of a jet stream at 250 mb, but the height of the tropopause was rather higher than one would expect. In contrast, Danielsen and Mohnen (1977) reported lower tropopause levels when O_3 recordings were high, as shown in Fig. 6.

The jet stream with high intensity would enhance a downward motion in the cyclogenetic area, particularly in the west side of an upper trough. The downdrafts could bring O_3 -rich air to the ground level along the west side of a frontal surface (note Fig. 4 and also the classical polar-front model of Bjerknes (1918)). The meteorological conditions described here are favourable for stratospheric O_3 intrusions into the PBL at Regina. The highest O_3 peak of 138-228 ppb occurred during a short period of only three hours around midnight. In contrast, daily O_3 maxima in warm seasons usually take place during the afternoon and high O_3 values observed during summer days often persist for several hours when anthropogenic precursors are main causative agents.

It should also be noted that high, or close to 60 ppb, O_3 values were not recorded at any up or downstream stations in the vicinity of Regina. The localized high values recorded at Regina did not normally occur in the province even during the summer months, and it was very unusual to observe them in winter. Moreover, anthropogenic emissions from Regina and its neighboring industrial

areas are relatively small in comparison to the emissions from other source regions. From these considerations and according to the meteorological data scrutinized it is now conclusive that the measured high values at Regina were the result of stratospheric O₃ intrusions to the ground level. Also, the observed high O₃ values at Regina and associated meteorological conditions appear to agree well with studies carried out by Attmannspacher and Hartmannsgruber (1973), Lamb (1977), Reiter et al. (1977) and Haagenson et al. (1981) as described earlier in Section 4(a).

Although the frequencies of passages of upper cold lows and troughs and of jet streams over the Great Lakes region and the Hudson Bay area are very high, the occurrence of stratospheric O₃ intrusions, resulting in high values at the surface, is an uncommonly observed phenomenon. According to Singh et al. (1980) and to Danielsen's concept, stratospheric intrusions should occur with the passage of each upper trough of high intensity. As noted earlier, the O₃ maximum in the ozonosphere is over the north section of Hudson Bay. Since intrusions are typically 100-300 km wide and several hundreds of kilometers long (Singh et al., 1980), it was anticipated that with the frequent passages of intense cyclones exceptionally high O₃ levels induced by ozonospheric air should be reported more commonly in northern Ontario and western Quebec, particularly during spring, winter and fall.

Moreover, a large-scale motion system including subsidence progresses continually, at least for several days. Therefore, it is not clear why exceptionally high O₃ values occur only scarcely and only at one location. Presumably, the swath of the ozonospheric air intrusion with continuous sinking is narrow and very small in comparison with the overall downslope motion along the cold frontal surface; the Regina recordings suggest that a surface O₃ peak occurs during the short period (1-3 hours) of impulsive downdrafts of O₃-rich air within the air columns of general subsidence. In addition, it may also be plausible that once the stratospheric air mass is forced to descend into the PBL, the O₃-rich air becomes extremely unstable

and it will no longer be in the photochemical equilibrium state. The statically unstable O_3 of stratospheric origin in the PBL must then initiate and destroy itself very quickly during a period of 1-3 hours, with chemical components of NO_x , OH, HO_2 , CH_4 etc. (eqns (4) in Section 2). In contrast, when high O_3 concentrations exceeding 100 ppb result from industrial precursor emissions, the warm season O_3 episodes in the PBL tend to last for several hours.

Present O_3 destruction schemes implicitly suggest that a significant amount (~ 70 ppb) of O_3 measured at the 4-5 km altitude of the troposphere might also have resulted from photochemical precursors of natural and anthropogenic origin of that level, excluding the high O_3 cases found in the vicinity of upper troughs. Apart from the polluted urban atmosphere in the PBL, the tropospheric photochemistry of ozone is not well understood. Over the last several years, there is some observational evidence of a gradual increase in concentrations of mid-tropospheric ozone, and it is suggested (Mateer, 1973) that there is a net production of ozone in the "free" troposphere.

6. SUMMARY AND CONCLUDING REMARKS

A review of the literature on atmospheric O_3 has been carried out. According to the research carried out during the last three decades, in general O_3 in the atmosphere can be said to have three origins with the greatest amount of O_3 apparently generated in the lower stratosphere. Stratospheric O_3 is transported into the upper troposphere and O_3 is also formed in the upper and mid-troposphere; evidence also indicates that O_3 is generated by photochemical precursors of natural and anthropogenic origins in the PBL. Estimations of stratospheric O_3 intrusions into the PBL indicate that concentrations of natural O_3 are generally less than 35 ppb, or in the range of 20-50 ppb at the ground which are well below the hourly Air Quality Standard level for both Canada (80 ppb) and the United States (120 ppb).

An examination of meteorological and O₃ data obtained at Regina, Saskatchewan indicated that stratospheric O₃-rich air was responsible for exceptionally high peak values of 228 ppb recorded at ground level. A typical stratospheric intrusion occurred with a characteristic duration of only 1-3 hours. The present observations agree well with the physical interpretations given by earlier reports. It is now clear that the stratospheric O₃ intrusions into the PBL with resulting short term concentrations of O₃ exceeding 120 ppb do occur at the "local" scale. The occurrence is not a common phenomenon even though favourable conditions for such ozonospheric intrusions appear to be present frequently in eastern North America. In some cases, anomalous O₃ readings might have been discounted as due to instrument malfunction and have been rejected in the process of data quality control and screening. It is suggested, therefore, that further studies should be carried out to determine the frequency of extremely high O₃ values recorded at other locations.

7. REFERENCES

1. Aldaz, L., 1969: Flux measurements of atmospheric ozone over land and water. J. Geophys. Res., 74, 6943-6946.
2. Attmannspacher, W., and R. Hartmannsgruber, 1973: On extremely high values of ozone near the ground. Pure Appl. Geophys., 106-108, 1091-1096.
3. Bjerknes, J., 1918: On the structure of moving cyclones. Geofys. Publ., 1, Oslo, 1-8.
4. Calvert, J.G., 1976: Test of the theory of ozone generation in Los Angeles atmosphere. Environ. Sci. Tech., 10, 248-256.
5. Chameides, W., and J.C.G. Walker, 1973: A photochemical theory of tropospheric ozone. J. Geophys. Res., 78, 8751-8760.
6. Chapman, S., 1930: A theory of upper atmospheric ozone. Mem. R. Meteor. Soc., 3, 103-125.
7. Chung, Y.S., 1976: Photochemical ozone and regional transport of air pollutants in the boundary layer. Proc. Int. Joint Symp. on Atmospheric Ozone - I.U.G.G., Dresden, Germany, Vol. III, 121-144.
8. Chung, Y. S., 1977: Ground-level ozone and regional transport of air pollutants. J. Appl. Meteor., 16, 1127-1136.
9. Chung, Y.S., and E.R. Reinelt, 1973: On lee cyclogenesis in the lee of the Canadian Rocky Mountains. Arch. Met. Geoph. Biokl., Ser. A, 22, 205-226.
10. Cleveland, W.S., B. Kliner, J.E. McRae and J.L. Warner, 1976: Photochemical air pollution: Transport from the New York City area into Connecticut and Massachusetts. Science, 191, 179-181.
11. Coffey, P.E. and W.N. Stasiuk, 1975: Evidence of atmospheric transport of ozone into urban areas. Environ. Sci. Tech., 9, 59-62.
12. Crutzen, P.J., 1974: Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air. Tellus, 26, 47-57.
13. Danielsen, E.F., 1968: Stratospheric-tropospheric exchange based on radioactivity, ozone and potential vorticity. J. Atmos. Sci., 25, 502-518.
14. Danielsen, E.F., 1980: Stratospheric source for unexpectedly large values of ozone measured over the Pacific Ocean during GAMETAG, August 1977. J. Geophys. Res., 85, 401-412.

15. Danielsen, E.F., and V.A. Mohnen, 1977: Project dustorm report: ozone transport, in situ measurements, and meteorological analyses of tropopause folding. J. Geophys. Res., 82, 5867-5877.
16. Davies, D.D., G. Smith and G. Klauber, 1974: Trace gas analysis of power plant plumes via aircraft measurements: O₃, NO_x and SO₂ chemistry, Science, 186, 733-735.
17. Dutkiewicz, V.A., and L. Husain, 1979: Determination of stratospheric ozone at ground level using ⁷Be/ozone ratios. Geophys. Res. Lett., 6, 171-174.
18. Dütsch, H.U., 1969: Atmospheric ozone and ultraviolet radiation. World Survey of Climatology, 4, D.F. Rex, Ed., Elsevier, 383-432.
19. Dütsch, H.U., 1978: Vertical ozone distribution on a global scale. Pure Appl. Geophys., 116, 511-529.
20. Dütsch, H.U., and C.C. Ling, 1973: Fourteen-year series of vertical ozone distribution over Arosa, Switzerland, from Umkehr measurements. Pure Appl. Geophys., 106-108, 1139-1150.
21. Fabian P., and C.E. Junge, 1970: Global rate of ozone destruction at the earth's surface. Arch. Met. Geoph. Biokl., Ser. A, 19, 161-172.
22. Fabian, P., and P.G. Pruchniewicz, 1977: Meridional distribution of ozone in the troposphere and its seasonal variations. J. Geophys. Res., 82, 2063-2073.
23. Fishman, J. and P.J. Crutzen, 1978: the origin of ozone in the troposphere. Nature, 274, 855-858.
24. Junge, C.E. 1962: Global ozone budget and exchange between stratosphere and troposphere. Tellus, 14, 363-377.
25. Junge, C.E., 1963: Air Chemistry and Radioactivity. Academic, New York.
26. Haagenson, P.L., M.A. Shapiro and P. Middleton, 1981: A case study relating high ground level ozone to enhanced photochemistry and isentropic transport from the stratosphere. J. Geophys. Res., 86, C6, 5231-5237.
27. Hering, W.S., 1966: Ozone and atmospheric transport processes. Tellus, 18, 329-336.
28. Hov, Ø, 1983: One-dimensional vertical model for ozone and other gases in the atmospheric boundary layer. Atmos. Envir., 17, 535-549.

29. Husian, L., P.E. Coffey, R.E. Meyers and R.T. Cederwall, 1977: Ozone transport from stratosphere to troposphere. Geophys. Res. Lett., 4, 363-365.
30. Johnson, W.B., and W. Viezee, 1981: Stratospheric ozone in the lower troposphere - I. Presentation and interpretation of aircraft measurements. Atmos. Envir., 15, 1309-1323.
31. Johnston, H., and G. Whitten, 1973: Instantaneous photochemical rates in the global stratosphere. Pure Appl. Geophys., 106-108, 1468-1489.
32. Lamb, R.G., 1977: A case study of stratospheric ozone affecting ground-level oxidant concentrations. J. Appl. Meteor., 16, 780-794.
33. London J., R.D. Bojkov, S. Oltmans and J.I. Kelly, 1976: Atlas of the Global Distribution of Total Ozone, July 1957 - June 1967. TN113 + STR, Nat. Cent. Atmos. Res., Boulder, Colorado, 276 pp.
34. Ludwick, J.D., T.D. Fox and L.L. Wendell, 1976: Ozone and radionuclide correlations in air of marine trajectory at Quillayute, Washington. J. Air Poll. Cont. Assoc., 26, 565-569.
35. Lusi, M.A., K.G. Anlauf, Y.S. Chung and H.A. Wiebe, 1976: Aircraft O₃ measurements in the vicinity of Toronto, Canada. Preprint 69th Annual Meeting Air Poll. Cont. Assoc., Portland, Oregon, No. 76-7.1, 14 pp.
36. Mateer, C.L., 1983: Personal Communication.
37. Nastrom, G.D., 1977: Vertical and horizontal fluxes of ozone at the tropopause from the first year of GASP data. J. Appl. Meteor., 16, 740-744.
38. Palmén, E., and C. Newton, 1969: Atmospheric Circulation Systems. Academic Press, 540 pp.
39. Reiter, E.R., H.J. Kanter, R. Reiter and R. Sladkovic, 1977: Lower-tropospheric ozone of stratospheric origin. Arch. Met. Geoph. Biokl., Ser. A, 26, 179-186.
40. Ripperton, L.A., H.E. Jeffries and J.J.B. Worth, 1971: Natural synthesis of ozone in the troposphere. Environ. Sci. Tech., 5, 246-248.
41. Samson, P.J. and K.W. Ragland, 1977: Ozone and visibility reduction in the Midwest: Evidence for large-scale transport. J. Appl. Meteor., 16, 1101-1106.
42. Schjoldager, J., 1979: Observations of high ozone concentrations in Oslo, Norway, during the summer of 1977. Atmos. Envir., 13, 1689-1696.

43. Schlesinger, M.E., and Y. Mintz, 1979: Numerical simulation of ozone production, transport and distribution with a global atmospheric general circulation model. J. Atmos. Sci., 36, 1325-1361.
44. Schönbein, C.F., 1840: Recherches sur la nature de l'odeur se manifeste dans certains actions chimiques. C.R. Acad. Sci., Paris, 10, 706.
45. Seinfeld, J.H., 1977: Correspondence. Envir. Sci. Tech., 13, 1218-1219.
46. Singh, H.B., W. Viezee, W.B. Johnson and F.L. Ludwig, 1980: The impact of stratospheric ozone on tropospheric air quality. J. Air Poll. Cont. Assoc., 30, 1009-1017.
47. Stallard, R.F., J.M. Edmond and R.E. Newell, 1975: Surface ozone in the South East Atlantic between Dakar and Walvis Bay. Geophys. Res. Lett., 2, 289-292.
48. Stickse, P.R., 1975: The stratosphere as a source of surface ozone. Preprint 68th Annual Meeting Air Poll. Cont. Assoc., Boston, Mass., No. 75-07.6, 10 pp.
49. Viezee, W., and H.B. Singh, 1980: The distribution of Beryllium-7 in the troposphere: Implications on stratospheric/tropospheric air exchange. Geophys. Res. Lett., 7, 805-808.
50. WMO, 1982: The Stratosphere 1981 - Theory and Measurements. WMO Ozone Report No. 11.
51. Wolff, G.T., M.A. Ferman and P.R. Monson, 1979: The distribution of beryllium-7 within high-pressure systems in the eastern United States. Geophys. Res. Lett., 6, 637-639.
52. Yap, D., and Y.S. Chung, 1977: Relationship of ozone to meteorological conditions in southern Ontario. Preprint 70th Annual Meeting Air Poll. Cont. Assoc., Toronto, Ont., No. 77-20.4, 16 pp.

Table 1 Summary of flights during which detailed measurements were obtained within intrusions

Selected Case No.	Date (1978)	Time (CST)	Approximate location of measurements*	Maximum ozone concentration (ppb)	Altitude (km ASL) of ozone maximum
1	12 May	11.27-15.16	HYS-CSM	312	7.3
	12 May	16.01-20.19	CSM-EMP	362	7.3
	13 May	14.34-19.19	MSL-MEI	318	7.3
	17 May	16.16-21.00	ABQ-GJT	282	6.9
2	18 May	09.13-13.43	RKS-GJT	299	7.3
3	19 May	13.11-17.40	GFK-FFM	231	7.3
4	5 Oct	17.15-21.37	CMI-MEM	161	7.3
	10 Oct	11.00-13.45	SUX-LNK	117	7.0
	14 Oct	11.54-16.52	STL-MEM	201	7.5
	30 Oct	15.46-19.11	INL-MSP	123	5.2

* ABQ = Albuquerque, New Mexico; CSM = Clinton, Oklahoma; EMP = Emporia, Kansas; FFM = Fergus Falls, Minnesota; GFK = Grand Fork, N. Dakota; GJT = Grand Junction, Colorado; HYS = Hays City, Kansas; CMI = Champaign, Illinois; INL = International Falls, Minn.; LNK = Lincoln, Nebraska; MEI = Meridian, Mississippi; MEM = Memphis, Tennessee; MSL = Muscle Shoals, Alabama; MSP = Minneapolis, Minnesota; RKS = Rock Springs, Wyoming; STL = St. Louis, Missouri; SUX = Sioux City, Iowa.

(from Johnson and Viezee, 1981)

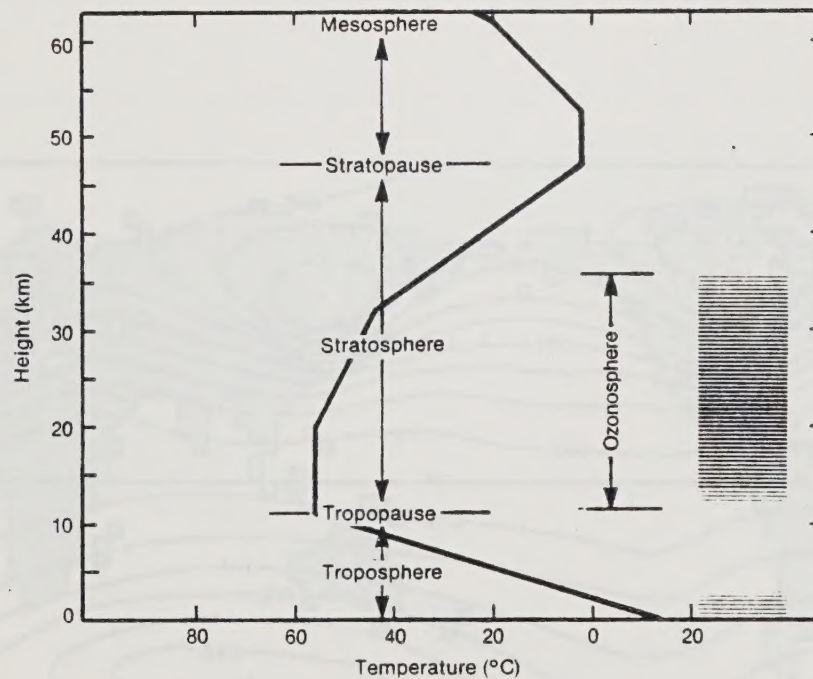


Fig. 1. Thermal structure of the atmosphere and distribution of ozone.

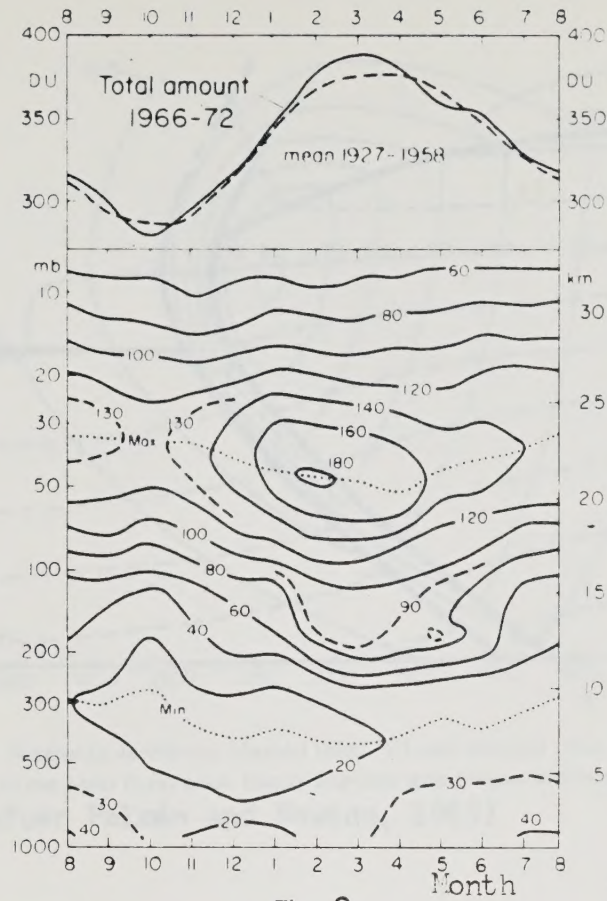


Fig. 2.

Mean time cross-section of vertical ozone distribution constructed from 6 years of observation. For comparison the seasonal variation of total ozone for the same observations is shown and also for the long-term mean

(After Dötsch and Ling, 1973)

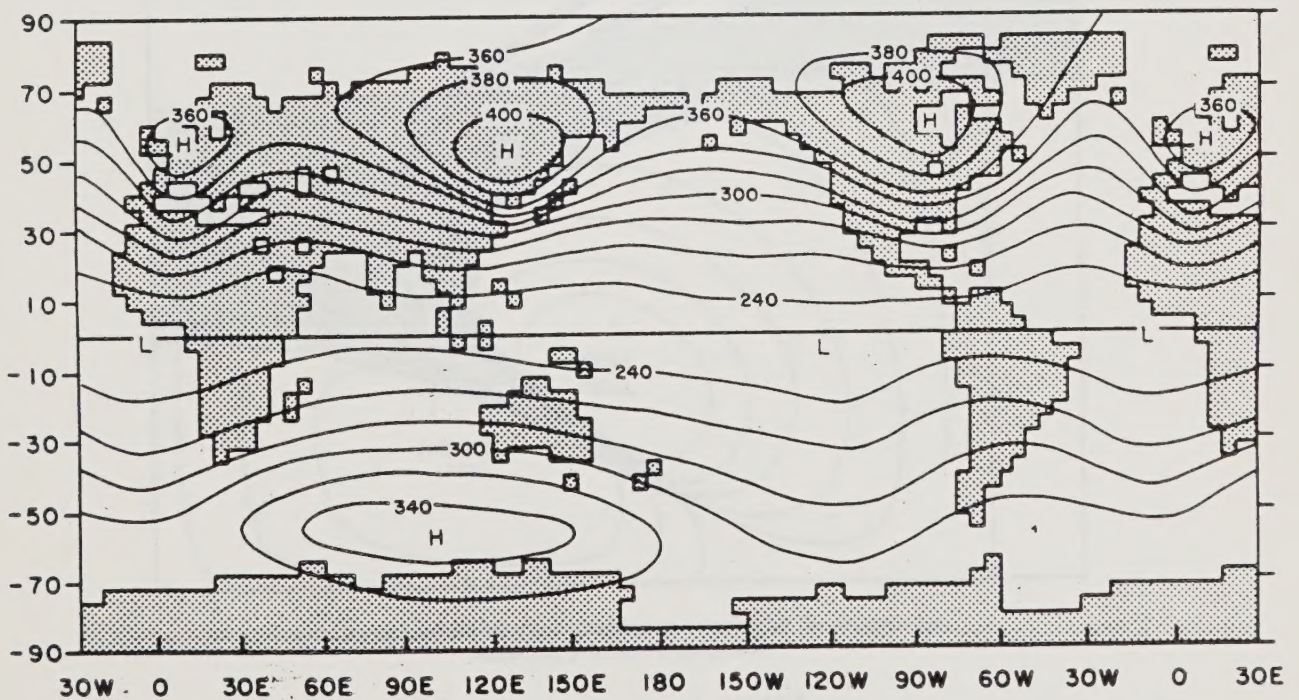


Fig. 3. Observed January 10-year mean of total ozone (in Dobson units).
(After London et al., 1976).

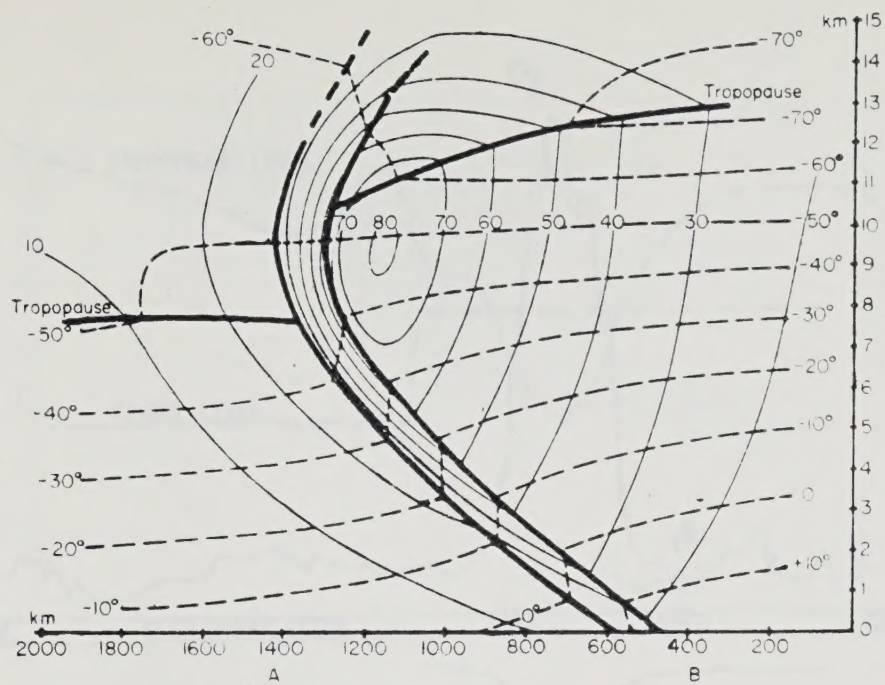


FIG. 4. Schematic isotherms (dashed lines, °C) and isotachs (thin solid lines, meters per second) in the polar front zone. Heavy lines are tropopauses and boundaries of frontal layer. (After Palmen and Newton, 1969)

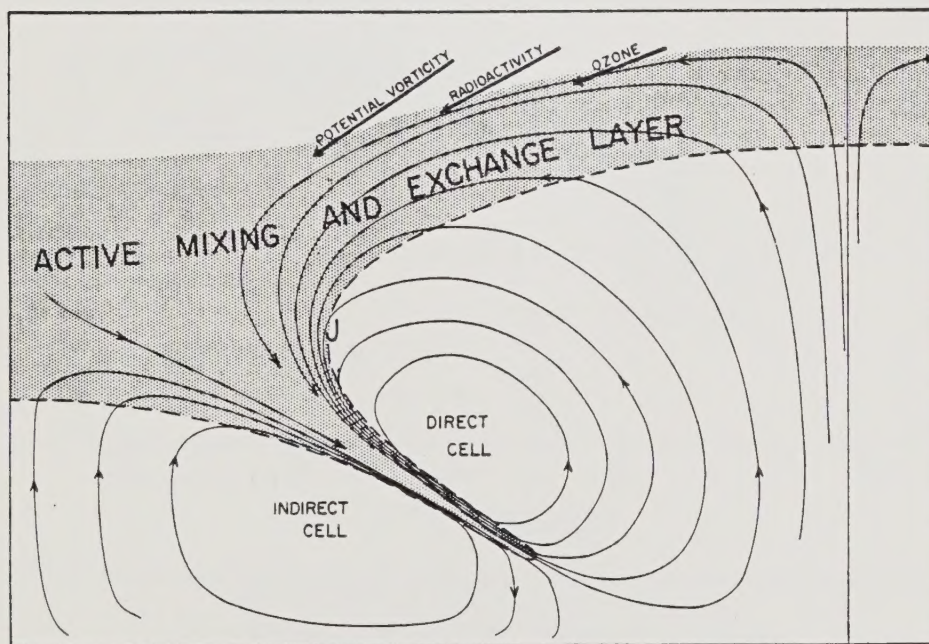


FIG. 5. Schematic of mean circulation relative to the tropopause, including a folded tropopause.

(After Danielsen, 1968)

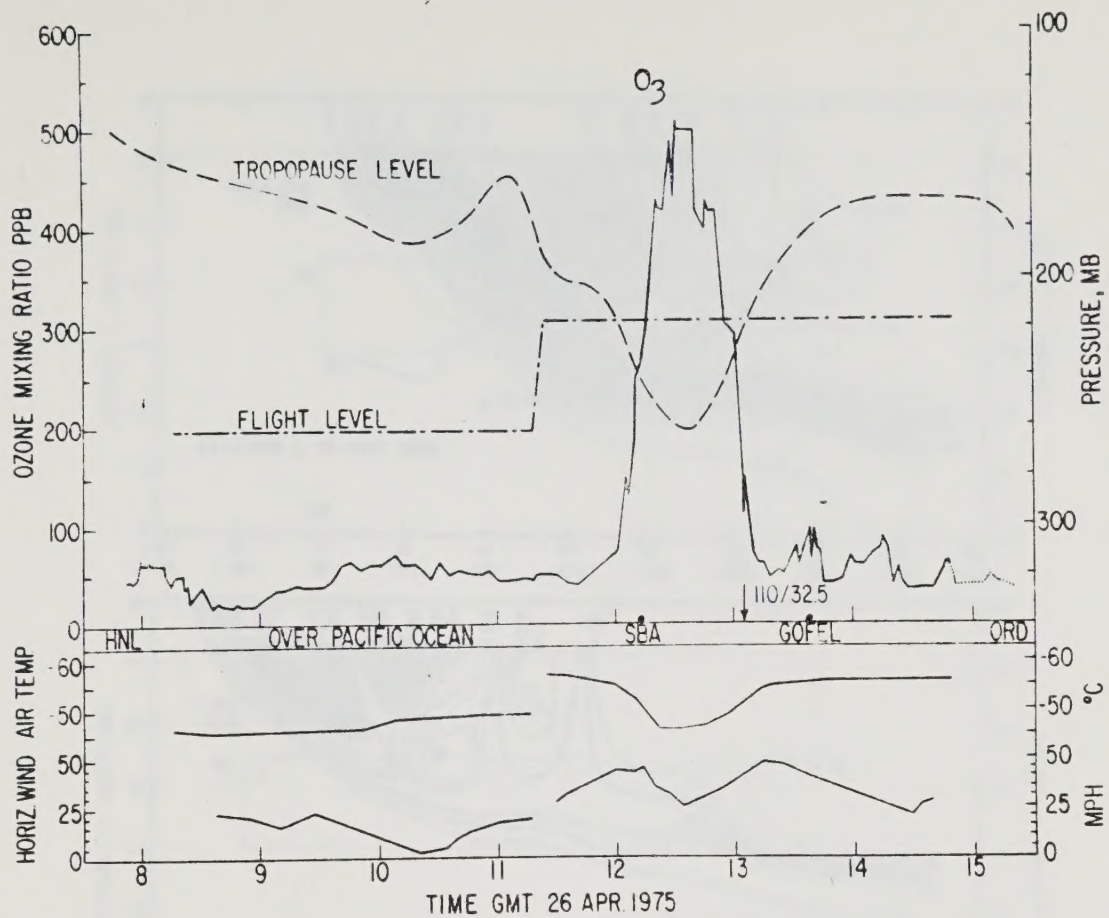


Fig. 6. Measurements from commercial aircraft above jet core.
(After Danielsen and Mohnen, 1977)

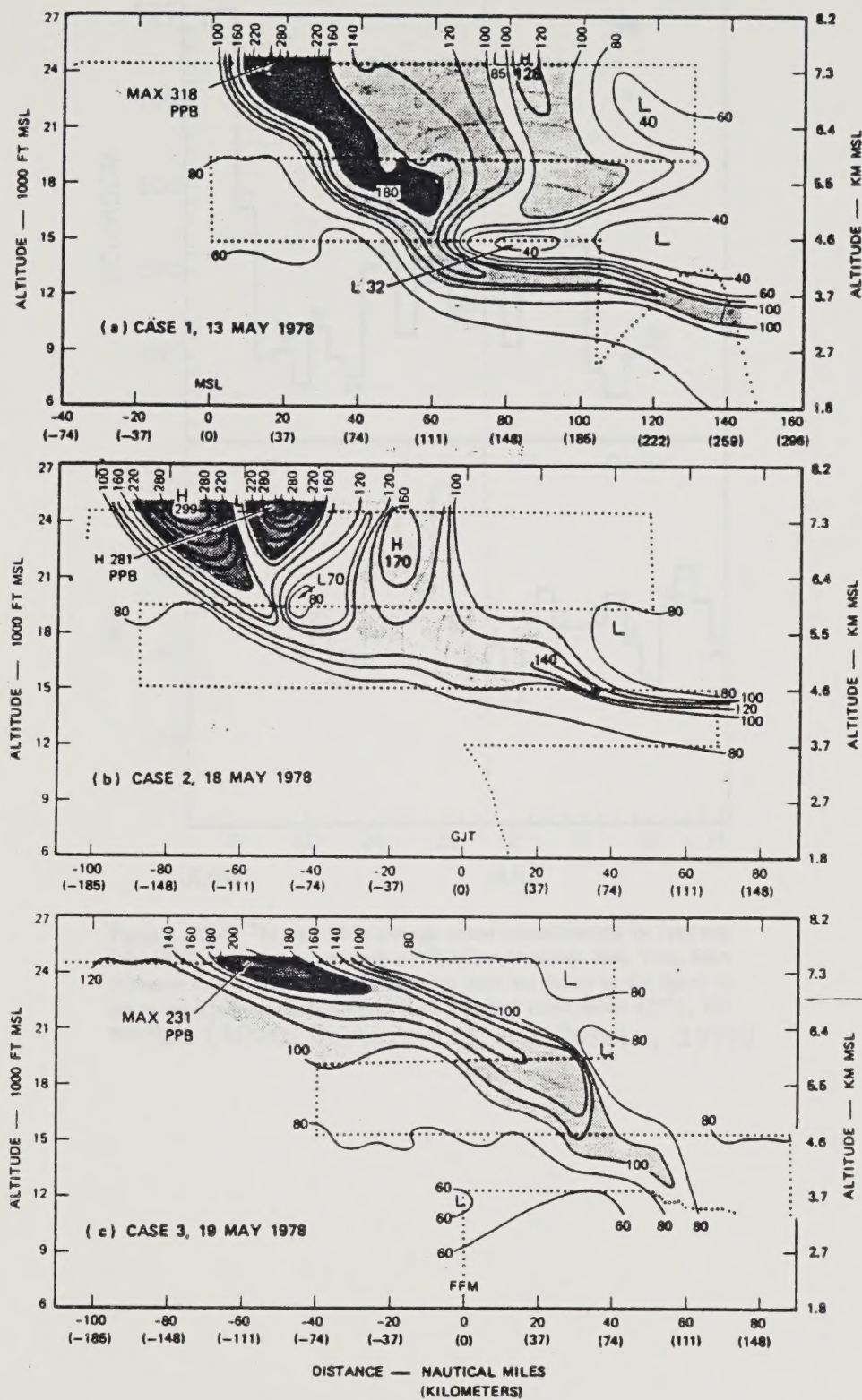


Fig. 7. Vertical cross-sections of measured ozone concentrations (ppb) for three cases in spring 1978. Aircraft flight paths are shown as dotted lines.
(from Johnson and Viezee, 1981)

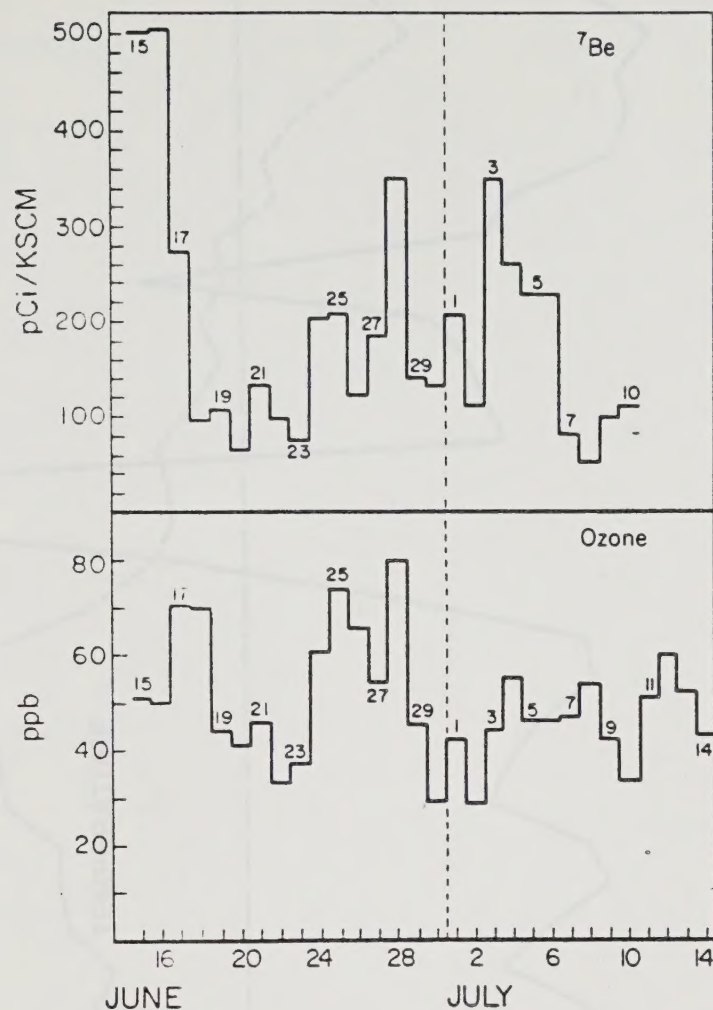


Figure 8. Daily ^7Be and 24-hr average ozone concentrations for June and July 1977 at the 1.5-km summit of Whiteface Mountain, New York. Stars represent lower-limit estimates. Selected days are shown in the figure to aid in intercomparisons. KSCM = kilo standard cubic meter (25°C , 760 mm Hg). (After Duktiewicz and Husain, 1979)

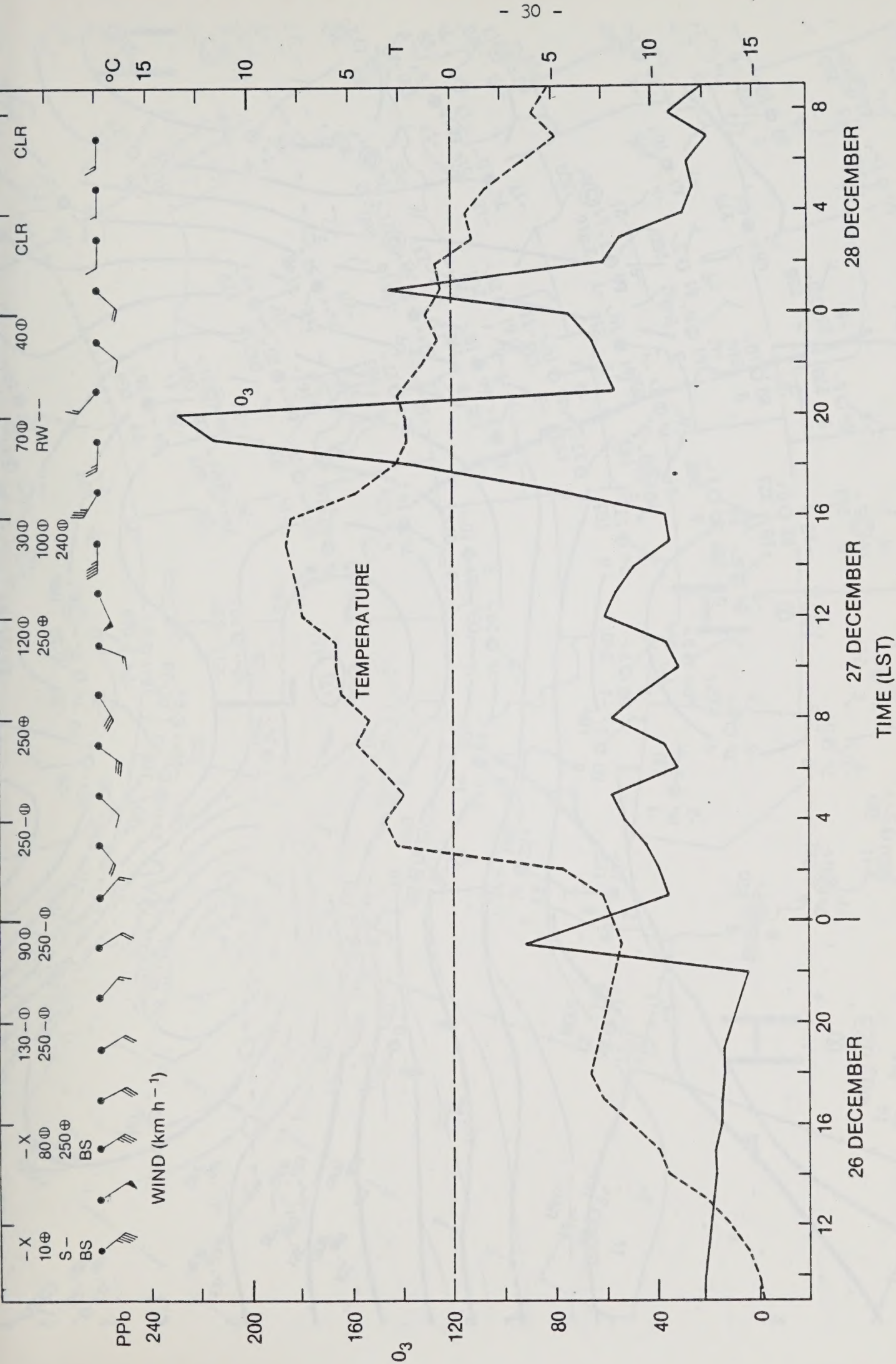


Fig. 9. Exceptionally high O₃ values recorded at Regina, Saskatchewan during 26-28 December 1980. Also included are ceiling of clouds (x 100 ft), weather phenomena, winds and air temperature.

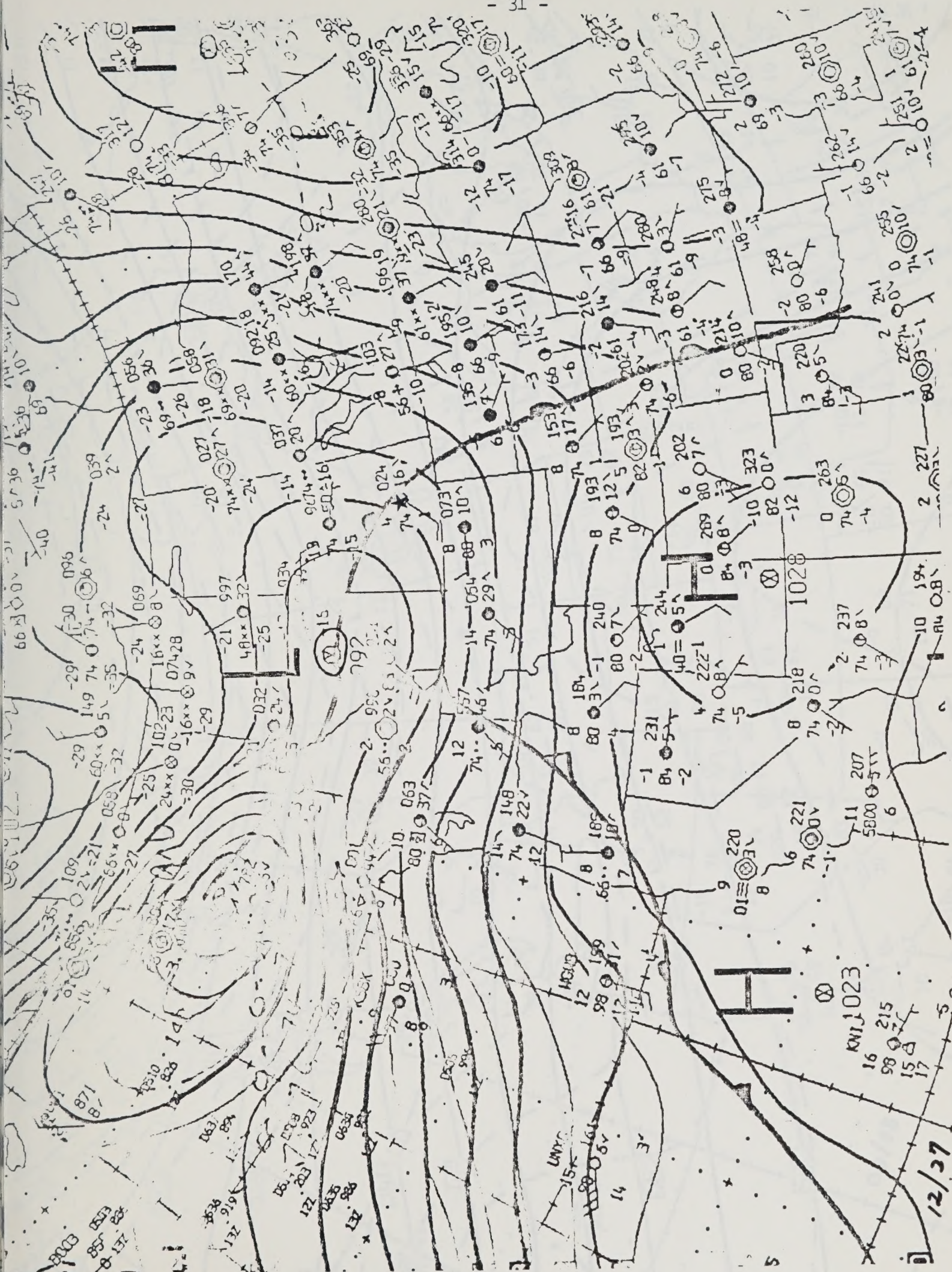


Fig. 10. Surface analysis for 0600 CST, 27 December 1980.

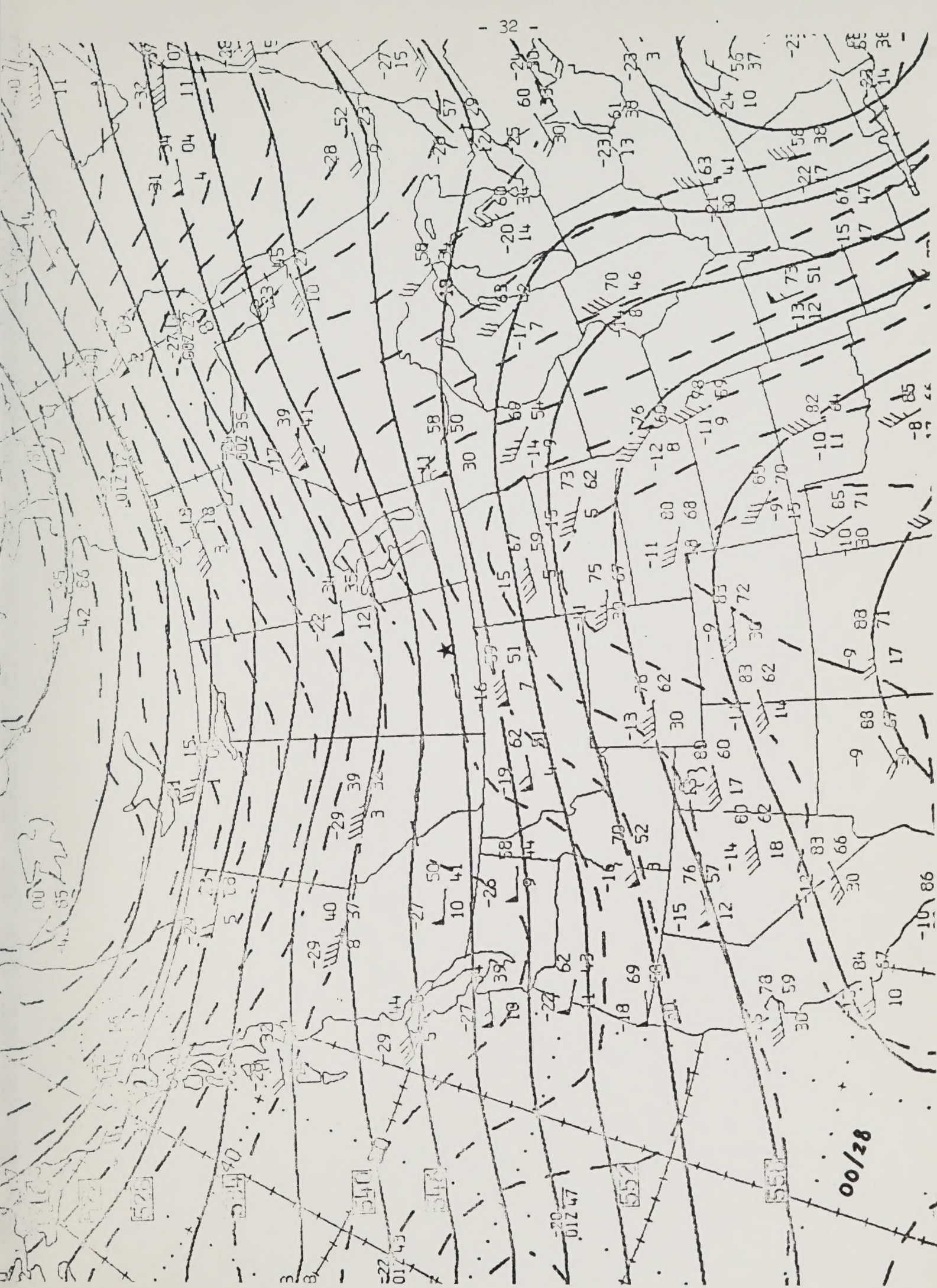


Fig. 11. 500 mb analysis for 1800 CST, 27 December 1980.

*Three Dark Figures
Making the Weather
In Folk, in Myth, in Legend,
A threefold test.
Shiva, Vishnu, Brahmin.
Father, Son, Holy Ghost.
Body, Mind, Spirit.
Triune, Triumvirate, Tribunal.
One is Isolate
Two is divisive
Three is Peace.
Three is Torment.
Three is Potent.
Power, Power, Power.
Air, Fire, Water.
Three Dark Figures,
Making the Weather.*

Ron Baird, Sculptor